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(54) Recovery of Oil from Tar Sands

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BACKGROUND OF THE INVENTIONField of the Invention

This invention relates to a process for recovering oil from tar sands. More particularly, the invention relates to a process whereby tar sands are extracted with water to produce a froth layer containing bitumen, water, sand and clay followed by pyrolysis of the dried froth to produce a liquid oil product.

Description of the Prior Art

Among the many approaches considered for separating the hydrocarbon fraction from tar sands, the aqueous extraction process represents a well-developed recovery technique. Typically, the tar sands are contacted with hot or cold water to extract the bitumen which is thereafter diluted with naphtha, allowed to settle and then centrifuged to remove residual solids. After removal of the diluent, the bitumen is fed to a pyrolysis unit wherein the bitumen is heated to form distilled and cracked products including vaporized liquid oil products, normally gaseous products and carbon which is deposited on solids present in the pyrolysis zone.

One of the principle disadvantages of the tar sands hot and cold water extraction processes is the enormous volume of aqueous tailings. These tailings contain a stable suspension of inorganic fines. Since no economically viable schemes have been devised for removing these suspended fines, the tailings are held in sludge ponds which are both a major expense and potentially an environmental hazard.

A further disadvantage of the aqueous extraction process is the loss of oil present as adhered organic matter in the finely divided clay which is in admixture with the separated sands. The presence of organics in these clays is reported in Energy and Fuels 1988(3) 386-391.

Various solvent extraction schemes have been proposed as alternatives to the aqueous extraction of tar sands. For example, Hanson discloses in U.S. Patent No. 4,071,433 a liquid slurry process for extracting tar sands in which the tar sands are slurried with an oil and divided in a centrifuge into streams containing course and fine sands. The fine sands stream is fed to a coker where the fines act as a nuclei in coke formation. The course sands stream is filtered by means of a hot oil filter and subsequently dried. Similarly, Irani et al disclose in U.S. Patent No. 4,036,732 the use of a C<sub>5</sub>-C<sub>9</sub> paraffin hydrocarbon solvent for the countercurrent extraction of tar sands.

Other references describe a non-extraction method for removing oil by the direct distillation of oil from bituminous sand in a fluidized solids bed. For example, Peterson and Gishler describe in The Petroleum Engineer, April, 1951, at pages 66-74 a fluidized solids technique for recovering oil from Alberta bituminous sand. In this process, raw bituminous sand is fed into a fluidized solids bed to distill and crack the bitumen present in the bituminous sand.

A review of the various known processes for recovering oil from tar sands is given by Chrones and Germain in their article entitled Bitumen and Heavy Oil Upgrading in Canada, Fuel Science and Technology International, 7(5-6), 783-821(1989).

SUMMARY OF THE INVENTION

A process for producing hydrocarbons from tar sands which comprises:

(a) contacting the tar sands with water to extract bitumen therefrom by forming (i) a froth layer containing bitumen, water and solids including sand and clay having adhered organic matter, (ii) an aqueous layer and (iii) precipitated, relatively bitumen-free sands;

(b) introducing the froth layer without substantial removal of solids therefrom into a pyrolysis zone wherein the solids in the froth layer are fluidized and the bitumen and organic matter are heated thereby forming vaporized liquid oil products, normally gaseous products and carbon which is deposited on the solids present therein;

(c) heating the carbon-containing solids from the pyrolysis zone in a combustion zone in the presence of oxygen to form hot solids and hot flue gas; and

(d) introducing the hot solids from the combustion zone into the pyrolysis zone to supply heat for the pyrolysis of the bitumen and other organic matter present therein.

In a preferred embodiment, the froth layer from the water extraction zone is dried to remove water prior to introduction into the pyrolysis zone and the hot flue gas from the combustion zone is used to supply heat for drying the froth layer.

The process of the present invention avoids or reduces the principle disadvantages resulting from hot water extraction, cold water extraction solvent extraction or pyrolysis of raw, i.e., unextracted tar sands. Pyrolysis of the froth layer without substantial removal of the fine clay solids contained therein reduces the volume of aqueous tailings containing a stable suspension of these fines. Further, introduction of the clay fines into the pyrolysis zone results in an increased hydrocarbon liquid yield. The present invention also avoids the expense and inconvenience of using organic solvents. The present invention also substantially reduces the amount of sands which must be handled in the pyrolysis zone, as contrasted with fluidized bed retort processes utilizing raw tar sands.

#### Brief Description of the Drawing

The Figure is a schematic illustration of a preferred embodiment of the invention.

#### Detailed Description of the Invention

The process of the invention is conveniently understood by reference to the Figure which schematically depicts a preferred embodiment. The description is given for purposes of illustration and is not intended to limit the invention thereto.

In the Figure, raw tar sands fed by line 12 are conventionally mixed in Extraction Zone 10 with water, steam (optional), air and a chemical reagent, such as a polyethylene glycol sold under the trade designation D-250 by Dow Chemical Company, which are introduced via lines 14, 16, 18, and 20 respectively. The chemical reagent serves as a surface active agent or dispersant and includes materials such as

polyglycols, polyethylene glycol or methyl isobutyl carbinol. A further description of these chemical reagents is given in a paper entitled "Experience in the Beneficiation of Two Alabama Tar Sands" by C. W. Schultz, J. B. Cardoso and G. Daniel Irvin and presented at the 1989 Eastern Oil Shale Symposium, November 15-17, 1989 Institute for Mining and Minerals Research, University of Kentucky, incorporated herein by reference. In general, water is mixed with the tar sands in the Extraction Zone at a weight ratio of 5:1 to 1:5, e.g. a 1:1 weight ratio.

The water temperature employed for extraction in Extraction Zone 10 may range from about 32°F - 212°F, preferably from about 36°F - 70°F, e.g., about 40°F. The conditions in the Extraction Zone cause small globules of bitumen to form. The resulting thick liquid slurry is then sent via line 22 to Primary Separation Zone 24 where most of the bitumen rises to the surface as a froth layer containing primarily bitumen with lesser amounts of water and solids including sand and clay having adhered organic matter. Typically, the froth layer will contain about 50 - 95, e.g., 60, weight percent bitumen, about 5 to 50, e.g., 20, weight percent water, about 1 to 25 weight percent sand and about 5 to 35 weight percent clay, e.g., 20 weight percent solids. The clay in the froth layer will typically contain about 0.5 to 10 weight percent of organic matter based on the weight of clay and organic matter. The froth layer from Primary Separation Zone 24 is sent via lines 26 and 28 to Dryer 30 which is heated by steam (not shown) for removal of water via line 32. The bottom layer in Primary Separation Zone 24 comprises excess water and precipitated sand having a small amount of adhered bitumen.

In between the froth layer and the precipitated sand and excess water is a mixture of clay, bitumen and water called "middlings". The middlings, excess water and precipitated sand are removed via line 34 and sent to Secondary Separation Zone 36 supplied with injected air via line 38 to remove the remaining bitumen which is thereafter sent to Dryer 30 via lines 40 and 28. Sand and water are removed from Secondary Separation Zone 36 via line 42 and sent to a tailings pond.

The dried froth from Dryer 30 is introduced by lines 44 and 46 into a pyrolysis zone such as a fluid coker or fluid bed retort. In the Figure, the pyrolysis zone is Fluid Coker 48.

In Fluid Coker 48, the dried froth is contacted with a fluidizing gas, such as steam, introduced via line 50 and hot fluidized solids consisting mainly of hot coked sand and carbon particles. The bitumen and other organic matter undergo extensive cracking and distillation on contact with the hot fluid bed and the cracking products and distillable portion of the bitumen feed flow up through a cyclone (not shown) to remove entrained solids which are returned to the coking zone through a dipleg (not shown). Vapors from the Fluid Coker leave the cyclone and pass into Scrubber 52 mounted on the coking reactor. The products boiling, for example, below 975°F (atmospheric pressure) comprising vaporized liquid oil products, and normally gaseous products are withdrawn via line 54 for fractionation in a conventional manner. Products boiling above 975°F may be recycled to the Fluid Coker via lines 56 and 46.

Coke produced in the Fluid Coker is deposited therein on fluidized sand and coke which are sent via

line 58 to Heater 60. The coked solids from the Fluid Coker are heated in the Heater in the presence of oxygen introduced via line 62 to form hot solids and hot flue gas. The hot solids from the Heater are introduced into the Fluid Coker via line 64 to supply heat for the pyrolysis of the bitumen and other organic matter present in the Fluid Coker. Flue gas from the Heater is withdrawn via line 66. Coke, sand and clay may be withdrawn from Fluid Coker 48 via line 68 or from Heater 60 via line 70. In a preferred embodiment, flue gas from the Heater is used for indirect contact with water to make steam which can be used to supply heat to Dryer 30.

The conditions in Fluid Coker 48 and Heater 60 are adjusted to provide a proper heat and materials balance in accordance with known conditions such as, for example, disclosed in U.S. Patents 4,055,484; 4,057,487 and 4,077,869 which are incorporated herein by reference.

By way of example, the fluidizing gas is admitted at the base of the Fluid Coker in an amount sufficient to obtain superficial fluidizing gas velocity in the range of 0.5 to 5 feet per second. The temperature in the Heater is maintained usually in the range of 1050 - 1500°F so that the heated solids are at least 100°F higher than the temperature in the Fluid Coker. Heated solids from the Heater are admitted to the Fluid Coker in an amount sufficient to maintain the pyrolysis temperature in the range of about 850° to about 1050°F. The pressure in the Fluid Coker may be maintained in the range of about 5 to about 150 lbs. per square inch (psig), usually in the range of about 5 to about 45 psig. Coked solids from the Fluid Coker are heated with sufficient air in the Heater to attain the desired temperature.



The process and advantage of the invention are further illustrated by the following.

EXAMPLE I

Athabasca bituminous sand from Alberta, Canada is extracted with toluene using a Dean-Stark separator to determine the bitumen, i.e., toluene soluble hydrocarbons present therein. The toluene-bitumen solution is then evaporated to drive off the toluene and isolate the bitumen. It is found that the bituminous sand contains about 10 weight percent bitumen on a dry basis.

The toluene insoluble solids are separated according to particle size and analyzed and found to have the analysis shown in the following Table 1.

Table 1

TOLUENE INSOLUBLE SOLIDS CONTAIN ORGANICS

<u>Fraction</u>	<u>Wt% of Solids</u>	<u>Wt% Organics</u>
Sand(1)	91.6	0.0
Clay(2)	7.8	6.8

(1) 44-250 microns

(2) below 44 microns

It is seen from the above table that bituminous sands contain a significant portion of organics in addition to the bitumen. Most of this organic matter adheres to the clay fines which are ordinarily discarded as a result of aqueous extraction of the bituminous sands, followed by solvent dilution of the bitumen layer and settling out of the solids.

In accordance with the present invention, the clay fines present in the bitumen layer following extraction (i.e., the froth layer containing primarily bitumen with lesser amounts of water, sand and clay) are retained along with the bitumen and sand for processing in a fluid coker or retort. Inclusion of the fine clays in the pyrolysis zone results in an increase in the amount of oil recovered from the bituminous sands. Further, reducing the level of clay which would otherwise be discarded with the aqueous stream reduces the volume of aqueous tailings containing a stable suspension of clay fines.

#### EXAMPLE II

A sample of Athabasca oil sands was Soxlet extracted in conjunction with a Dean-Stark separator with boiling toluene. The resulting assay was (all in weight percent): bitumen 11.50, solids 87.47, and water 1.03. The solids were wet sieved to separate them into various size fractions. The material passing through the finest sieve, 635 US Std. Mesh, was centrifuged to obtain two fractions, a sediment layer called the -635 mesh fraction, and an unsettled solid identified as Suspended Fines. The fraction of organic material on each fraction was also determined. These data are shown in Table 2. For this particular sample, the toluene insoluble organics represented about 5 weight percent of the total organic material in the oil sand. For oil sands containing more fines (defined as material passing 325 mesh) the amount of toluene insoluble organics is larger and represents a larger fraction of the total organics in the oil sand.

Table 2

Toluene Insoluble Organics in Whole  
Athabasca Oil Sand

<u>Solids Mesh</u> <u>Size US Std</u> <u>Sieve</u>	<u>Wt% of</u> <u>Total</u>	<u>Wt% Organic</u> <u>in Fraction</u>	<u>Wt% Organic of</u> <u>Total in Oil Sand</u>
+60	0.82	6.13	0.34
-60/+200	78.81	0.0	0.0
-200/+325	1.06	1.28	0.11
-325/+635	0.92	1.29	0.10
-635	4.29	6.31	2.24
Susp. Fines	1.57	16.90	2.20
Total	87.47	---	4.99

EXAMPLE III

To further illustrate the invention, a sample of bitumen froth from cold water froth flotation of Athabasca oil sands was allowed to settle into two layers, the analysis of which is shown in Table 3. The upper, bitumen layer was bitumen rich and contained 6.14 weight percent solids insoluble in boiling toluene, the balance being bitumen. The lower, sediment layer was solids rich, containing 63.31 weight percent solids insoluble in boiling toluene. Of the remaining 36.69 weight percent, 21.95 weight percent was bitumen and 14.74 weight percent was water. The upper and lower layers comprised 48 and 52 weight percent, respectively, of the total bitumen froth sample. The solids from the respective layers, after washing with boiling toluene, were wet sieved as discussed above. The particle size distributions and organic contents of the solids in the two layers are shown below in Table 3. The toluene insoluble organic material represented 4.4 weight percent of the total organics in the bitumen froth sample.

Table 3

Bitumen Froth Solids

Solids Mesh Size	<u>Sediment Layer</u>		<u>Bitumen Layer</u>	
	<u>Wt%</u>	<u>Wt% Organic</u>	<u>Wt%</u>	<u>Wt% Organic</u>
+60	1.40	35.25	-	-
-60/+80	2.19	6.84	-	-
-80/+120	13.15	3.99	-	-
-120/+200	29.88	2.12	-	-
-200/+325	18.46	4.00	7.33	21.04
-325/+635	13.77	7.16	10.59	20.31
-635	19.79	11.16	64.49	21.67
Susp. Fines	1.36	17.28	17.59	16.95
Layer Assay				
Wt% Solids		63.31		6.14
Wt% Bitumen		21.95		93.86
Wt% Water		14.74		0.0
Layer wt% of Total Sample		52		48
Layer Solids Wt% of Total Solids		92		8
Layer Solids Organics, Wt% of Organics in Solids		76.3		23.7
Layer Solids Organics, Wt% of Total Organics		3.4		1.0

EXAMPLE IV

The solids fractions of Example III were subjected to pyrolysis at 525°C to determine the fraction of the toluene insoluble organic material converting to coke and volatile products. The data are shown below in Table 4. In general, the fraction of organic converting to coke decreased with decreasing solid particle size, with the exception to the suspended fines fraction from the sediment layer. By combining the information in Tables 3 and 4, the total yield of coke and volatile products from the pyrolysis of the toluene insoluble organic material present on the solids can be determined. This is shown in Table 5. A total of 75.2 weight percent of volatile products were obtained by pyrolysis of the toluene insoluble organic material from the froth sample.

Table 4

Pyrolysis of Insoluble Organics in  
Bitumen Froth Solids

<u>Mesh Size</u>	<u>Sediment Layer</u>		<u>Wt% Coke/Wt% Organic</u>
	<u>Wt% Organic</u>	<u>Wt% Coke</u>	
+60	35.25	21.30	0.6043
-60/+80	6.84	3.49	0.5102
-80/+120	3.99	1.64	0.4110
-120/+200	2.12	0.28	0.1321
-200/+325	4.00	0.33	0.0825
-325/+635	7.16	2.12	0.2961
-635	11.16	1.18	0.1057
Susp. Fines	17.28	7.26	0.4201

<u>Bitumen Layer</u>			
-200/+325	21.04	12.82	0.6093
-325/+635	20.31	8.11	0.3993
-635	21.67	5.63	0.2598
Susp. Fines	16.95	6.69	0.3947

EXAMPLE V

In another test, a sample of Athabasca oil sand was extracted exhaustively with dichloromethane at ambient conditions. Analysis of the solids after extraction showed they contained about 0.9 weight percent insoluble organic material. The solids were then pyrolyzed in a continuous feed fluidized bed pyrolysis reactor at 510°C. The yield of volatile organic products was 65 weight percent of the organic material fed to the reactor.

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Table 5

VOLATILE ORGANIC YIELD FROM PYROLYSIS OF TOLUENE  
INSOLUBLE ORGANICS IN FROTH SOLIDS

Solids Sieve Size US <u>Standard Mesh</u>	Wt% of <u>Tot. Solid</u>	Wt% of Total Insol <u>Organic</u>	Conversion <u>to Volatiles</u>	Volatile Yield Wt% of Total <u>Insoluble Organics</u>
<u>Sediment Layer Solids</u>				
+60	1.29	6.29	0.3957	2.49
-60/+80	2.00	1.91	0.4898	0.94
-80/+120	12.11	6.70	0.5890	3.95
-120/+200	27.52	8.10	0.8679	7.03
-200/+325	17.01	9.44	0.9175	8.66
-325/+635	12.67	12.59	0.7039	8.86
-635	18.22	28.23	0.8943	25.25
Susp. Fines	0.96	3.01	0.5799	1.75
<u>Bitumen Layer Solids</u>				
-200/+325	0.60	1.77	0.3907	0.69
-325/+635	0.87	2.47	0.6007	1.48
-635	5.30	16.06	0.7402	11.89
Susp. Fines	1.45	3.43	0.6353	2.18
Total	100.00	100.00		75.17



THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for producing hydrocarbons from tar sands which comprises:

(a) contacting the tar sands with water to extract bitumen therefrom by forming (i) a froth layer containing bitumen, water, sand and about 5-35 wt.% clay having adhered organic matter, (ii) an aqueous layer and (iii) precipitated, relatively bitumen-free sands;

(b) introducing the froth layer without substantial removal of solids therefrom into a pyrolysis zone wherein the solids in the froth layer are fluidized and the bitumen and organic matter are heated thereby forming vaporized liquid oil products, normally gaseous products and carbon which is deposited on the solids present therein;

(c) heating the carbon-containing solids from the pyrolysis zone in a combustion zone in the presence of oxygen to form hot solids and hot flue gas; and

(d) introducing the hot solids from the combustion zone into the pyrolysis zone to supply heat.

2. The process of claim 1 wherein the froth layer is dried prior to its introduction into the pyrolysis zone.

3. The process of claim 2 wherein the hot flue gas from the combustion zone is used to supply heat to dry the froth layer.

4. A process for producing hydrocarbons from tar sands which comprises:

(a) contacting the tar sands with water to extract bitumen therefrom by forming (i) a froth layer containing bitumen, water, sand and about 5-35 wt.% clay having adhered organic matter, (ii) an aqueous layer and (iii) precipitated, relatively bitumen-free sands;

(b) separating the froth layer from the aqueous layer and the precipitated sand in a primary separation zone;

(c) introducing the froth layer without substantial removal of solids therefrom into a drying zone to remove water;

(d) introducing the dried froth into a pyrolysis zone wherein the dried froth is fluidized and heated to form vaporized liquid oil products, normally gaseous products and carbon which is deposited on the solids present therein;

(e) heating the carbon-containing solids from the pyrolysis zone in a combustion zone in the presence of oxygen to form hot solids and hot flue gas; and

(f) introducing the hot solids from the combustion zone into the pyrolysis zone to supply heat for the pyrolysis of the bitumen and other organic matter present therein.

5. The process of claim 4 wherein the tar sands and water in step (a) are contacted with air.

6. The process of claim 5 wherein the froth layer formed by the water extraction of tar sands contains about 50 to 90 weight percent bitumen, about 5 to 25 weight percent sand and about 5 to 35 weight percent clay having adhered organic matter.

7. The process of claim 6 wherein the clay present in the froth layer contains at least 1.0 weight percent organic matter based on the weight of clay and organic matter.

8. The process of claim 7 wherein there is present in the primary separation zone a middlings layer containing relatively less bitumen and relatively more water and clay than the froth layer.

9. The process of claim 8 comprising introducing the middlings layer and air into a secondary separation zone for recovery of bitumen.

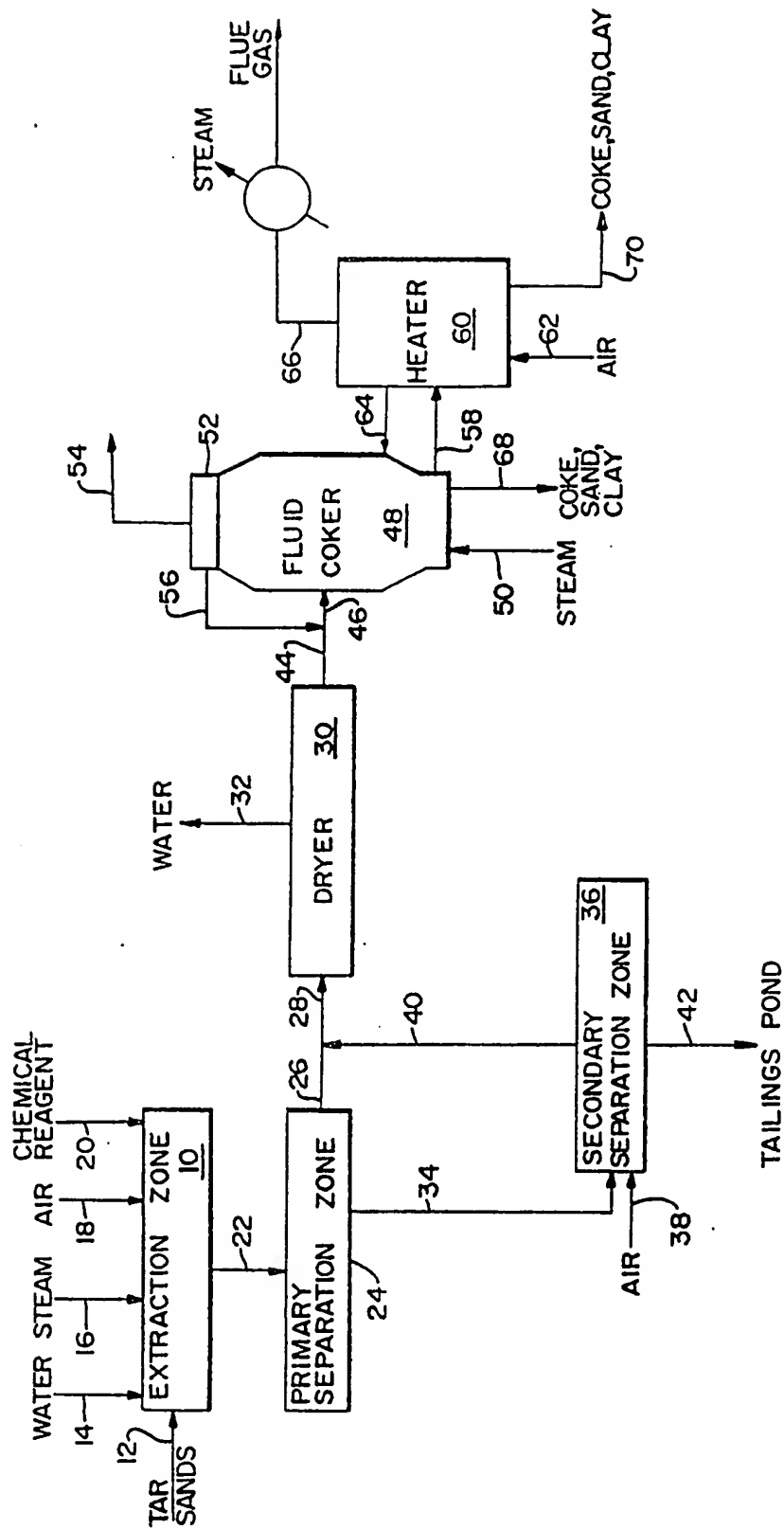
10. The process of claim 9 wherein bitumen from the secondary separation zone is combined with bitumen from the primary separation zone.

11. The process of claim 10 wherein the sand and clay solids in the froth layer are greater than 5 weight percent based on the total weight of the froth layer.

12. The process of claim 11 wherein the temperature of the water used to extract bitumen from the tar sands is in the range of about 70°F to 200°F.

13. The process of claim 11 wherein the temperature of the water used to extract bitumen from the tar sands is in the range of about 36°F to 70°F.

14. The process of claim 13 wherein the vaporized liquid oil products from the pyrolysis zone are separated into fractions boiling below and above about 975°F and the fraction boiling above about 975°F are recycled to the pyrolysis zone for conversion therein.



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